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An Integral Method of Non-Isothermal Kinetic Analysis

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16. Abstract A quantitative semianalytic solution for the constant heating rate Arrhenius integral forms the basis of a new isoconversion method for determining both the activation energy and frequency factor of an arbitrary, single-step reaction from temperature scanning experiments independent of the form of the rate law. Advantages of the new integral method compared to existing techniques include simplicity, better accuracy, and broad applicability.			
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EXECUTIVE SUMMARY

A semianalytic solution of the constant heating rate Arrhenius integral is the basis of a new isoconversion method for determining the activation energy and frequency factor of an arbitrary, single-step reaction from a series of temperature scanning experiments. No assumptions about the form of the rate law are necessary to apply the present integral method to the analysis of non-isothermal reaction data. Thermogravimetry data for a low-density polyethylene at various constant heating rates were analyzed using the new method and the activation energy $E_a = 200$ kJ/mol and the frequency factor $A = 2 \times 10^{11} \text{ s}^{-1}$ determined from the data for anaerobic pyrolysis were in the range of published values for this polymer under these conditions. The new isoconversion method was also used to analyze differential scanning calorimetry data for the curing reaction of phenylethynyl-terminated imide oligomers and provided an activation energy $E_a = 133$ kJ/mol in quantitative agreement with published work. A single value for the frequency factor was obtained for the phenylethynyl curing reaction using the present method $A = 1 \times 10^7 \text{ s}^{-1}$, which is well within the range $A = 10^4\text{--}10^9 \text{ s}^{-1}$ estimated from the original work.

The agreement of the Arrhenius activation energy and frequency factor for polyethylene pyrolysis and the phenylethynyl curing reaction determined by the present method with literature values for these quantities suggests the general utility of the simple new isoconversion integral method for determining kinetic parameters of single-step reactions from constant heating rate experiments. Determination of a physically meaningful reaction rate law from isothermal experiments is now possible since the Arrhenius rate constant can be obtained independent of any assumptions about reaction order or the form of the conversion function.

INTRODUCTION

Many technologically important processes and reactions occur under nonisothermal conditions and it is often desired to calculate or predict the progress of the reaction over time during transient heating. Integral methods of nonisothermal analysis utilize cumulative values of a species concentration, heat of reaction, weight loss, etc., measured in temperature scanning experiments to extract the kinetic parameters of a reacting system and determine a suitable rate law [1-13]. These powerful methods derive from the programmable heating rate capability of modern thermal analysis equipment and are useful for calculating preconversion during the heatup period in isothermal experiments [11], for testing reaction models over a broad temperature and conversion range [13], etc. Despite their utility however, integral methods have suffered from low sensitivity, a dependence on the form of the rate law, an assumption that the reaction mechanism does not change with temperature, and the somewhat cumbersome mathematics of the series approximations for the Arrhenius integral required in the analyses [3, 11]. An exact solution of the Arrhenius integral is possible only for nonlinear temperature programs [3], but this capability is beyond most commercial instruments.

Since the overwhelming majority of thermal analyses are conducted at constant heating rate, the present work seeks to develop a more useful approximation for the Arrhenius integral under experimental conditions of a linear temperature program and extend these results to the unambiguous determination of Arrhenius kinetic parameters. It is hoped that the results of this work will aid process development of new fire resistant thermoset resins and advance the study of polymer flammability by allowing more accurate calculation of the gasification rate in the pyrolysis zone of burning polymers [14]. Since the rate-limiting step in polymer pyrolysis is the breaking of primary chemical bonds in the molecule [15], a direct method for determining pyrolysis rate constants will facilitate the decoupling of diffusion and chemical kinetics during burning and help relate polymer structure to flammability.

BACKGROUND

Rate laws of the type

$$\frac{d\alpha}{dt} = f(\alpha, T) \quad (1)$$

are the basis for almost all of the kinetic methods used in differential thermal analysis and differential scanning calorimetry [1-13, 16]. In equation 1, T is the absolute temperature and is a

$$\alpha = \frac{C(t) - C(0)}{C(\infty) - C(0)}$$

fractional conversion in terms of the instantaneous, $C(t)$, initial, $C(0)$, and final, $C(\infty)$, values of a measurable reaction parameter such as a species concentration, heat of reaction, and pyrolyzed mass. Equation 1 is written such that α increases with time, t . The temperature dependence of $f(\alpha, T)$ is usually assumed to reside exclusively in a rate constant, k , which has the Arrhenius form

$$k = A \exp(-E_a/RT)$$

where A is the pre-exponential or frequency factor, E_a the activation energy for the reaction, and R the universal gas constant. These assumptions lead to the generalized reaction rate law

$$\frac{d\alpha}{dt} = k f(\alpha) \quad (2)$$

If k is independent of α and $f(\alpha)$ is independent of T , separation of variables in equation 2 gives

$$F(\alpha) \equiv \int_{\alpha_0}^{\alpha} \frac{d\alpha'}{f(\alpha')} = \int_0^t k dt' = \int_0^t A e^{-E_a/RT} dt' \quad (3)$$

where primed symbols denote variables of integration. At constant temperature, $F(\alpha) = kt$ which is the basis for isothermal kinetic analyses [1, 3, 11, 13, 17]. A variety of $f(\alpha)$ have been assumed or derived for individual cases [1, 4, 5, 13, 17] such that a linear $F(\alpha)$ versus time plot is obtained at a particular temperature having slope $k(T)$. The Arrhenius parameters A and E_a for the reaction are determined from a number of constant temperature experiments by plotting the natural logarithm of $k(T)$ versus $1/T$ over the temperature domain of interest.

The isothermal procedure based on equation 2 requires *a priori* knowledge of $F(\alpha)$, and the measured kinetic parameters are valid only for the temperature range examined. Usually $f(\alpha)$ and therefore $F(\alpha)$ are not known prior to the experiment so various methods have been proposed to allow determination of E_a and $f(\alpha)$ separately or in combination from a series of temperature-scanning experiments at different constant heating rates [1-3, 6-13]. For a constant heating rate, $dT/dt = \beta$, equation 3 can be written

$$F(\alpha) = \frac{A}{\beta} \int_{T_0}^T e^{-E_a/RT} dT' \quad (4)$$

where the sample temperature is uniform but changes linearly from T_0 to T over the time interval $(0, t)$. Application of nonisothermal or integral methods to experimental data requires evaluating the exponential temperature (Arrhenius) integral on the right hand side of equation 4. Unfortunately, the Arrhenius integral has no exact solution so numerical or approximate solutions are required.

Approximate solutions for the Arrhenius integral can be expressed in terms of the quantity $x = -E_a/RT$ so that equation 4 takes the form

$$F(\alpha) = \frac{AE_a}{\beta R} \int_{x_0}^x \frac{e^{x'}}{x'^2} dx' = \frac{AE_a}{\beta R} p(x') \Big|_{x_0}^x \quad (5)$$

Several series expansions have been used to represent $p(x)$ in equation 5 and Flynn and Wall provide an excellent review [3]. Typical of these series solutions is an asymptotic expansion of the exponential integral obtained from a single integration by parts [18], i.e.,

$$p(x) = \frac{e^x}{x^2} \left[1 + \frac{2!}{x} + \frac{3!}{x^2} + \frac{4!}{x^3} \dots \right] \quad (6)$$

and Schlomilch's expansion [19]

$$p(x) = \frac{e^x}{x(x-1)} \left(1 - \frac{1}{(2-x)} + \frac{2}{(2-x)(3-x)} - \frac{4}{(2-x)(3-x)(4-x)} + \dots \right) \quad (7)$$

A property of these integral expansions is that the difference between the true value of the function and the sum of a finite number of terms in the series is essentially of the order of magnitude of the last term retained. This requires that either $-x > 30$, or that a few terms be retained in the series expansions for $-x < 10$, to achieve an accuracy greater than 95%. An empirical equation for $p(x)$ was proposed by Doyle [6],

$$p(x) = 7.03 \times 10^{-3} e^{x B(x)} \quad (8)$$

where $B(x)$ ranges from 1.195 to 1.034 over the domain $x = -10$ to -60 . An average value, $B(x) = 1.052$, is often used in integral methods of thermal analysis [2, 3, 6, 8, 11, 13].

ARRHENIUS INTEGRAL APPROXIMATION

The intractability of multiterm series approximations required for accurate evaluation of the Arrhenius integral has limited the utility of integral methods for quantitative kinetic analysis. The following is a simple, semianalytic result which provides better accuracy than any previous single term approximation of the constant heating rate Arrhenius temperature integral.

Begin by defining a new variable, $y = e^x/x^2$, so that equation 4 becomes

$$F(\alpha) = \frac{AE_a}{\beta R} \int_{y_0}^y f(y') dy' \quad (9)$$

with $f(y) = x/(x-2)$. A single integration by parts gives

$$F(\alpha) = \frac{AE_a}{\beta R} \left\{ \left[\frac{e^{x'}}{x'(x'-2)} \right] \Big|_{x_0}^x + 2 \int_{x_0}^x \frac{e^{x'} dx'}{x'^2(x'-2)^2} \right\} \quad (10)$$

Repeated integration by parts transforms the right hand side of equation 10 into

$$F(\alpha) = \frac{AE_a}{\beta R} \frac{e^{x'}}{x'(x'-2)} \left[1 + \frac{2}{x'(x'-2)} + \frac{8}{x'^2(x'-2)^2} + O(x'^{-4}) + O(x'^{-5}) + \dots \right] \Big|_{x_0}^x \quad (11)$$

For the normal temperature ranges and activation energies of scanning thermal analysis, the lower limit in the final solution can be neglected since $-x_0 \gg -x$. Moreover, since $-x \geq 10$ (typically), only the first term of equation 11 need be retained

$$F(\alpha) \approx \frac{AE_a}{\beta R} \frac{e^x}{x(x-2)} = \frac{ART^2}{\beta(E_a + 2RT)} e^{-E_a/RT} \quad (12)$$

By way of comparison Doyle's approximation (equation 8) leads to the single-term result

$$F(\alpha) \approx 7.03 \times 10^{-3} \frac{AE_a}{\beta R} e^{-1.052 E_a/RT} \quad (13)$$

while the first term of the asymptotic expansion (equation 7) gives

$$F(\alpha) \approx \frac{AE_a}{\beta R} \frac{e^x}{x^2} = \frac{ART^2}{\beta E_a} e^{-E_a/RT} \quad (14)$$

Equation 12 differs from equation 14 by the factor $2RT$ in the denominator. Because of their simplicity, equations 13 and 14 are commonly used in integral methods of thermal analysis [1-3, 6-8, 11-13].

The relative percent error associated with the use of Doyle's approximation (equation 13) and the single term asymptotic expansion (equation 14) as solutions of the Arrhenius integral for a physically realistic domain of x are plotted in figure 1 along with the error for the present result, equation 12. The "exact" value of the Arrhenius integral used for the error calculation was obtained by double precision numerical integration of equation 4 using the trapezoidal rule with a step size of 0.5K between the limits: $T_0 = 300K$, T . Figure 1 shows that equation 12 is

significantly more accurate than either of the single-term approximations, equation 13 or equation 14, as a solution of the Arrhenius integral. Equation 12 under predicts the true value of the Arrhenius integral by less than 1% over the domain $-x \geq 10$ normally encountered in experimental studies. Comparable accuracy requires at least three terms of the asymptotic expansion or two terms of the Schlomilch expansion [20].

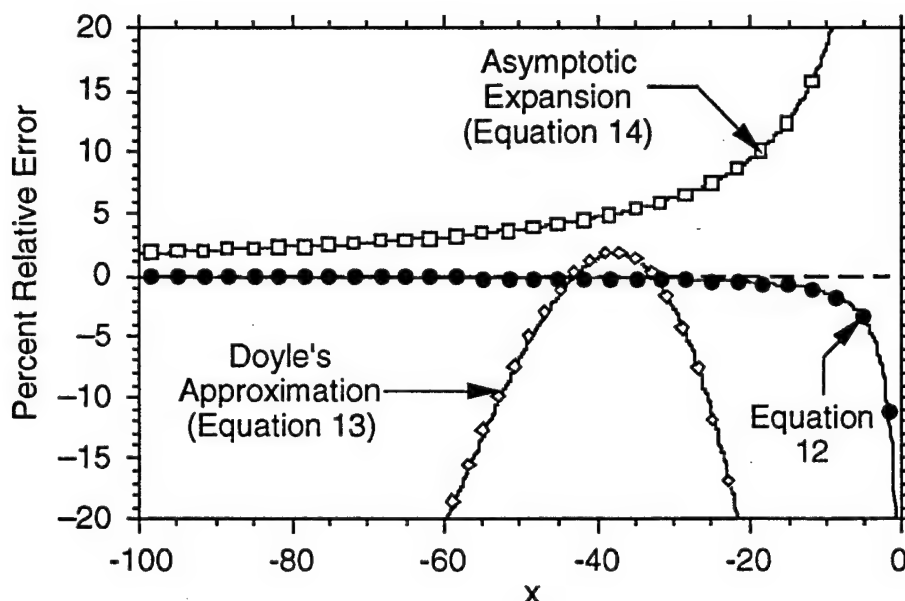


FIGURE 1. PERCENT RELATIVE ERROR *VERSUS* $x = -E_a/RT$ FOR EQUATIONS 12, 13, AND 14 AS APPROXIMATIONS FOR THE ARRHENIUS INTEGRAL

Figure 2 is a plot of the percent relative error *versus* temperature using equation 12 to approximate the Arrhenius integral for a range of activation energies. An accuracy of greater than 99% is obtained for $E_a \geq 100$ kJ/mol over the temperature range normally examined in scanning thermal analyses. The positive catastrophe in figure 2 at low temperatures is the result of neglecting the lower limit of integration in arriving at equation 12, which becomes significant as T approaches T_0 .

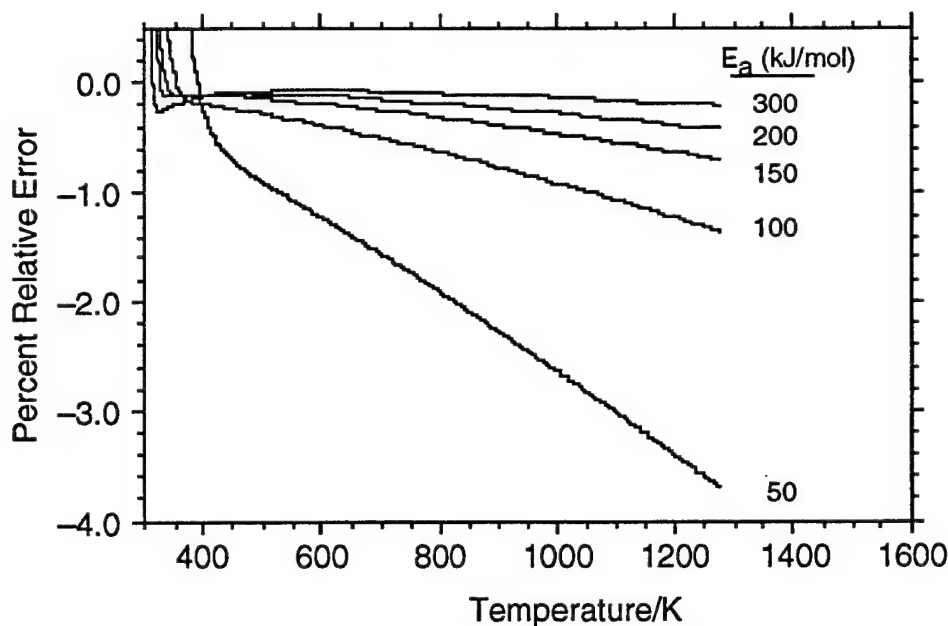


FIGURE 2. PERCENT RELATIVE ERROR VERSUS TEMPERATURE FOR EQUATION 12 WITH $E_a = 50, 100, 150, 200,$ AND 300 kJ/mol

ACTIVATION ENERGY FROM CONSTANT HEATING RATE EXPERIMENTS

The determination of both A and E_a from isothermal or nonisothermal experiments requires *a priori* knowledge of $f(\alpha)$ or $F(\alpha)$. A common functional form for $f(\alpha)$ is an arbitrary (n -th) order reaction [1,3–13, 17, 18] which allows an analytic solution for $F(\alpha)$ and provides an additional fitting parameter—the reaction order, n . However while A and E_a have physical significance [14], their numerical values and the reaction order determined from three-parameter fits of n -th order kinetics to conversion data is questionable except in the case of a well defined reaction mechanism [3]. To circumvent the need to assume n -th order reaction kinetics to extract kinetic parameters, isoconversion methods [2, 6, 8, 11, 12, 19] have been developed which utilize temperature and heating rate data at a fixed value of α and thus, presumably, a fixed value of $F(\alpha)$. This eliminates the need to assume a functional form for $F(\alpha)$ to determine the activation energy of the reaction but precludes simultaneous determination of the frequency factor. Typical of the isoconversion methods is an iterative technique for determining E_a directly from conversion *versus* temperature data at different heating rates proposed by Wall [2]. The method is based on Doyle's approximation of the Arrhenius integral (equation 13) which can be differentiated to give

$$\frac{d \ln \beta}{d \frac{1}{T(\alpha)}} \approx -B(x) \frac{E_a}{R}$$

where $T(\alpha)$ is the temperature corresponding to a specific degree of conversion at a particular heating rate. The method requires successive approximations of E_a as the empirical coefficient $B(x)$ is incremented for each new value of $E_a/RT(\alpha)$. The activation energy thus determined is independent of $F(\alpha)$ to the extent that the assumptions used to obtain equations 1-4 are valid but the method is tedious to apply and empirically based [1, 3].

An analogous but more direct method for determining E_a from constant heating rate experiments without any assumptions about the form of $f(\alpha)$ or its integral $F(\alpha)$ follows from equation 12. Taking the natural logarithms of equation 12

$$\ln [F(\alpha)] = \ln A - \ln \beta - \ln \frac{1}{T(\alpha)} - \ln (2-x) + x \quad (15)$$

where $x = x(\alpha) = -E_a/RT(\alpha)$. If $F(\alpha)$ and A are independent of temperature and β is treated as a continuous variable, equation 15 can be "differentiated" with respect to the reciprocal isoconversion temperature, $1/T(\alpha)$,

$$\frac{d \ln \beta}{d \frac{1}{T(\alpha)}} = -T(\alpha) \left[2 - x - \frac{2}{2-x} \right] \quad (16)$$

The $2/(2-x)$ term on the right hand side of equation 16 accounts for less than two percent of the bracketed quantity for $-x \geq 10$. Neglecting this term, the result for the slope of a plot of heating rate *versus* the reciprocal temperature at any fixed conversion is

$$\frac{d \ln \beta}{d \frac{1}{T(\alpha)}} = - \left[\frac{E_a}{R} + 2T(\alpha) \right] \quad (17)$$

from which the activation energy at a particular conversion is

$$E_a(\alpha) = -R \left[\frac{d \ln \beta}{d \frac{1}{T(\alpha)}} + 2T(\alpha) \right] \quad (18)$$

FREQUENCY FACTOR FROM CONSTANT HEATING RATE EXPERIMENTS

If the activation energy of the reaction is known (e.g., from equation 18) and β , $T(\alpha)$ data are available, then equation 15 is a single equation with two unknowns, A and $F(\alpha)$. Determination of a unique value for the frequency factor, A , from equation 15 therefore requires a numerical value for $F(\alpha)$. If $F(\alpha)$ satisfies the usual condition for the normalized conversion integral $F(\alpha) = 1$ at $\alpha = 1$ (cf. references 3, 17), then $\ln[F(\alpha)] = 0$ at completion of the reaction and equation 12 becomes for $T(\alpha=1) \equiv T(1)$

$$\ln [F(1)] = 0 = \ln[A] - \ln[\beta] - \ln\left[\frac{1}{T(1)}\right] - \ln\left[2 + \frac{E_a}{RT(1)}\right] - \frac{E_a}{RT(1)} \quad (19)$$

from which

$$\ln\left[\frac{\beta}{T(1)}\right] = \ln[A] - \left\{ \ln\left[2 + \frac{E_a}{RT(1)}\right] + \frac{E_a}{RT(1)} \right\} \quad (20)$$

Equation 20 states that a plot of $\ln[\beta/T(1)]$ *versus* the quantity $\{\ln[2 + E_a/RT(1)] + E_a/RT(1)\}$ at the incipient completion temperature of the reaction $T(1)$ has a slope equal to negative unity and an intercept of $\ln[A]$. The frequency factor is calculable by direct substitution of E_a and $\beta, T(1)$ data pairs into equation 20 after some rearrangement.

$$A = \frac{\beta \{E_a + 2RT(1)\}}{RT(1)^2} e^{E_a/RT(1)} \quad (21)$$

Alternatively, E_a may be used as a fitting parameter in equation 20 to obtain unit negative slope in a plot of $\ln[\beta/T(1)]$ *versus* $\{\ln[2 + E_a/RT(1)] + E_a/RT(1)\}$, yielding $\ln[A]$ as the intercept. The unit slope method allows simultaneous determination of both the global activation energy and frequency factor of an arbitrary single-step reaction from a few temperature scanning experiments without any assumptions about the reaction order or the functional form of $f(\alpha)$.

EXPERIMENTAL

POLYETHYLENE PYROLYSIS.

Table 1 is a compilation of fractional mass loss temperatures $T(\alpha)$ obtained in our laboratory for anaerobic pyrolysis of 3-5 mg samples of low-density polyethylene ($M_w \approx 35,000$ g/mol, $M_w/M_n = 4.5$, $\rho = 0.906$ g/cm³, Aldrich Chemical) under nitrogen in a thermogravimetric analyzer (Perkin Elmer TGA-7) at constant heating rates $\beta = 5, 10, 20, 40, 60$, and 80 K/min. Figure 3 is a composite of the data in table 1 plotted as $\ln[\beta]$ versus $1/T(\alpha)$ for volatile fractions $\alpha = 0.01, 0.02, 0.05, 0.10, 0.20, 0.50$, and 1.00 . High correlation coefficients ($r^2 > 0.98$) were obtained for all of the linear regression curves of $\ln[\beta]$ *versus* $1/T(\alpha)$ and the slopes at each conversion were used in equation 18 to calculate the activation energies plotted in figure 4 *versus* fractional conversion.

Individual values for the activation energy at each conversion calculated by equation 18 were within $\pm 0.2\%$ of the mean value plotted in figure 4 indicating that E_a determined by this method is essentially independent of temperature.

TABLE 1. HEATING RATE AND FRACTIONAL MASS LOSS TEMPERATURES FOR PYROLYSIS OF LOW-DENSITY POLYETHYLENE

Heating Rate	T(0.01)	T(0.02)	T(0.05)	T(0.10)	T(0.20)	T(0.50)	T(1.0)
K/min	K	K	K	K	K	K	K
5	639	655	680	695	711	726	762
10	658	678	699	715	730	749	779
20	673	691	712	726	740	761	792
40	689	706	727	741	756	776	808
60	699	713	734	749	764	784	821
80	709	723	744	758	773	793	833

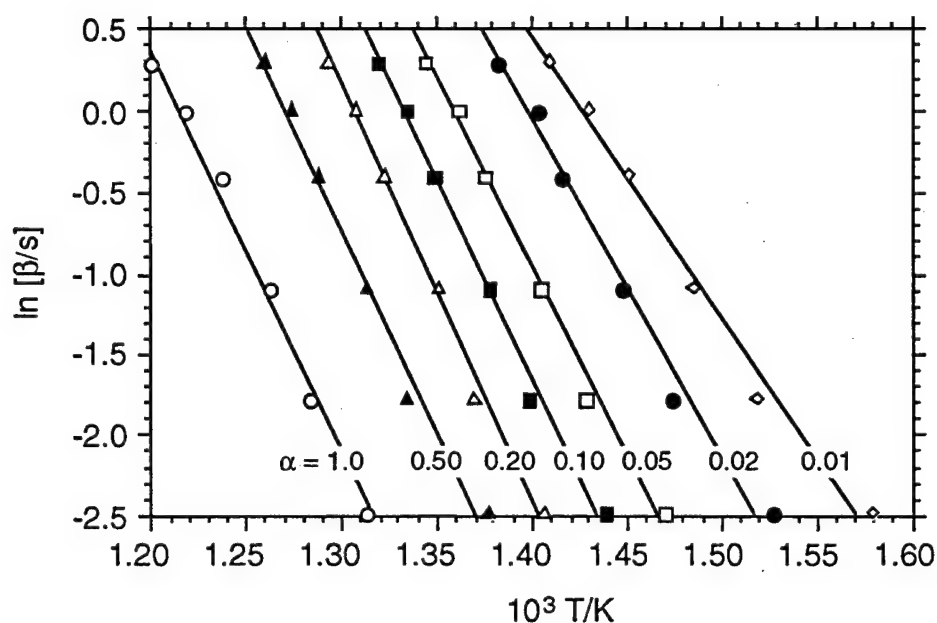


FIGURE 3. PLOT OF NATURAL LOGARITHM OF HEATING RATE *VERSUS* THE RECIPROCAL TEMPERATURE FOR VOLATILE FRACTIONS, $\alpha = 0.01, 0.02, 0.05, 0.10, 0.20, 0.50$, AND 1.0 FOR LOW MOLECULAR WEIGHT, LOW-DENSITY POLYETHYLENE

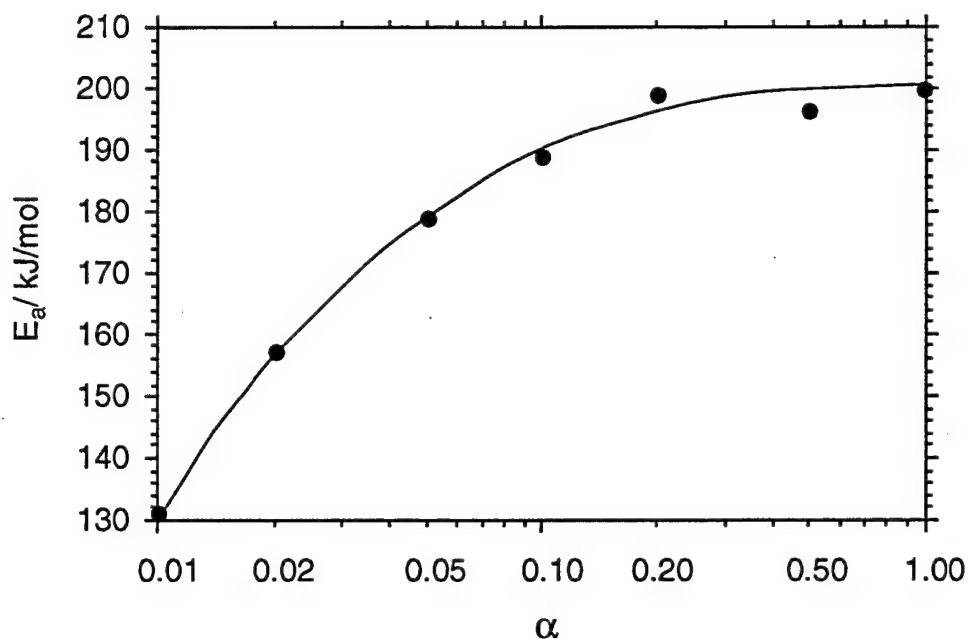


FIGURE 4. ACTIVATION ENERGY *VERSUS* FRACTIONAL WEIGHT LOSS FOR LOW-DENSITY POLYETHYLENE CALCULATED FROM EQUATION 18

The variation in activation energy with weight loss observed in figure 4 for low molecular weight, low-density polyethylene suggests the possibility of consecutive thermal degradation reactions or a single-step reaction with a distribution of activation energies over the conversion domain. Alternatively, $F(\alpha)$ or A may be temperature dependent so that their derivatives with respect to $1/T$ are nonzero as was assumed in deriving equation 18. The relatively constant value $E_a \approx 200$ kJ/mol for conversions above about twenty percent in figure 4 is within the range of literature values $E_a = 192\text{--}263$ kJ/mol reported for this polymer under these experimental conditions [21].

Figure 5 is a plot of the $T(1)$ data in table 1 according to equation 20 for the low-density polyethylene of this study. Unit negative slope in figure 5 was obtained for $E_a = 200$ kJ/mol in agreement with the method of equation 18 and figure 4. The correlation coefficient for the linear regression curve was $r^2 = 0.99$. The intercept of the linear plot in figure 5 is $26.039 = \ln[A]$ from which $A = 2.0 \times 10^{11} \text{ s}^{-1}$, a typical value for the frequency factor or pre-exponential term in polymer thermal degradation [13].

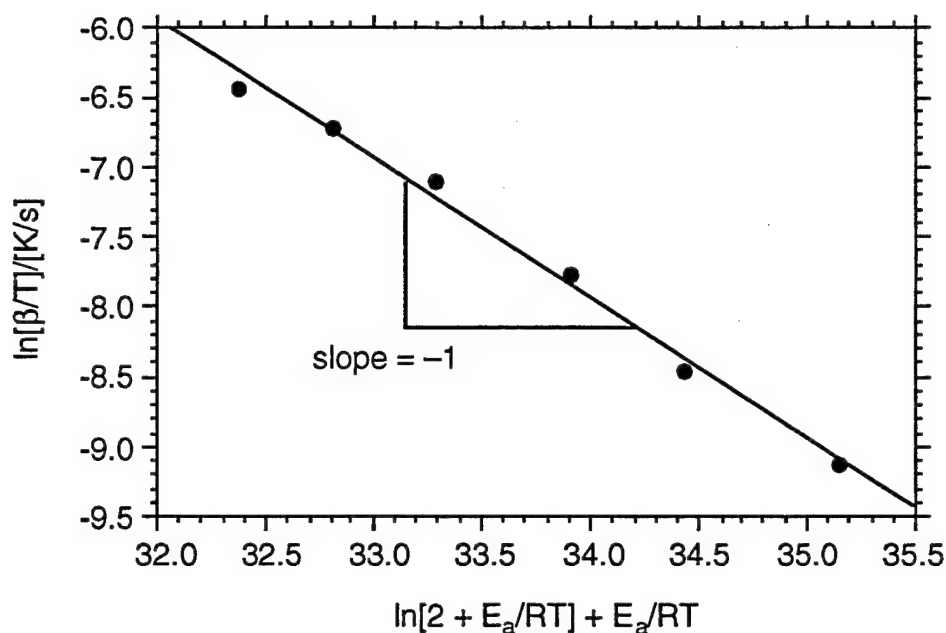


FIGURE 5. PLOT OF $\ln[\beta/T]$ VERSUS $\{\ln[2 + E_a/RT] + E_a/RT\}$ FOR THERMAL DEGRADATION OF LOW-DENSITY POLYETHYLENE AT COMPLETE CONVERSION ACCORDING TO EQUATION 20 WITH $E_a = 200$ kJ/mol

PHENYLETHYNYL CURING REACTION.

The present isoconversion integral method of nonisothermal kinetic analysis was also applied to differential scanning calorimetry data for the curing reaction exotherm of phenylethynyl-terminated imide oligomers obtained by Hinkley [22, 23]. These nonisothermal phenylethynyl curing experiments were conducted on approximately 7 mg samples of the oligomer in a differential scanning calorimeter (Shimadzu DSC-50) at heating rates of 5, 20, 40, 60, and 80 K/min. Samples of fine powder were contained in open platinum pans purged with nitrogen during the temperature scanning experiments. Fractional conversion, α , was calculated as the cumulative heat of reaction up to a particular temperature in the scanning experiments divided by the total heat of reaction at the incipient temperature of complete reaction according to standard methods [24].

Hinkley's analysis of these data using Wall's [2] isoconversion method and Doyle's integral approximation (equation 13) for $\alpha = 0.10, 0.30, 0.50$, and 0.90 yielded an average activation energy for the phenylethynyl curing reaction $E_a = 139.0 \pm 3.3$ kJ/mol. However for this activation energy and temperature range, $x = -E_a/RT \approx -(139 \text{ kJ/mol})/(8.314 \text{ J/mol-K})(800\text{K}) = -21$ and the more accurate empirical constant $B(x) = 1.098$ [2] should have been used in equation 13 in place of the average $B(x) = 1.052$. This second iteration of $B(x)$ as per Wall [2] improves the activation energy estimate for the phenylethynyl curing reaction to $E_a = 133.2 \pm 3.2$ kJ/mol which agrees well with studies by other investigators who had found $E_a = 132.3$ and 152.8 kJ/mol for the curing reaction of phenylethynyl-terminated model compounds [25]. Attempts by Hinkley to determine a single frequency factor for the phenylethynyl curing reaction were unsuccessful due to the presence of the two unknowns, $F(\alpha)$ and A in equation 13. Hinkley assumed n -th order kinetics with $n = 3/2$ and used the β -independent conversion value $\alpha \approx 0.48$ at the peak reaction rate temperature to

obtain a numerical value for $F(\alpha = 0.48)$. Substituting $F(0.48)$ into equation 13 resulted in a range of frequency factors $A = 10^4$ to 10^9 s^{-1} for the phenylethynyl curing reaction.

Hinkley's phenylethynyl curing data at complete conversion were not published in his original work [23] but were kindly provided and are given in table 2. Analysis of these data using equation 18 with the best-fit slope of the linear regression of $\ln[\beta]$ versus $1/T(1)$ gives an average $E_a = 132.8 \pm 0.6 \text{ kJ/mol}$. Substituting $E_a = 132.8 \text{ kJ/mol}$ into equation 21 gives $A = 9.8 \pm 0.8 \times 10^6 \text{ s}^{-1}$ for the five data pairs. By comparison, the unit negative slope method (equation 20) plotted in figure 6 gives $E_a = 133.4 \text{ kJ/mol}$ and $A = 10.7 \times 10^6 \text{ s}^{-1}$ with a correlation coefficient $r^2 = 0.992$. These activation energies for the phenylethynyl curing reaction determined from equations 18 and 20 are self-consistent and in quantitative agreement with the published values while the frequency factors for this reaction determined from equation 20 and 21 are well within the estimated range for this Arrhenius parameter.

TABLE 2. HEATING RATE AND INCIPIENT COMPLETION TEMPERATURES FOR PHENYLETHYNYL CURING REACTION [23]

Heating Rate, K/min	5	20	40	60	80
$T(\alpha=1)$, K	726	778	795	810	821

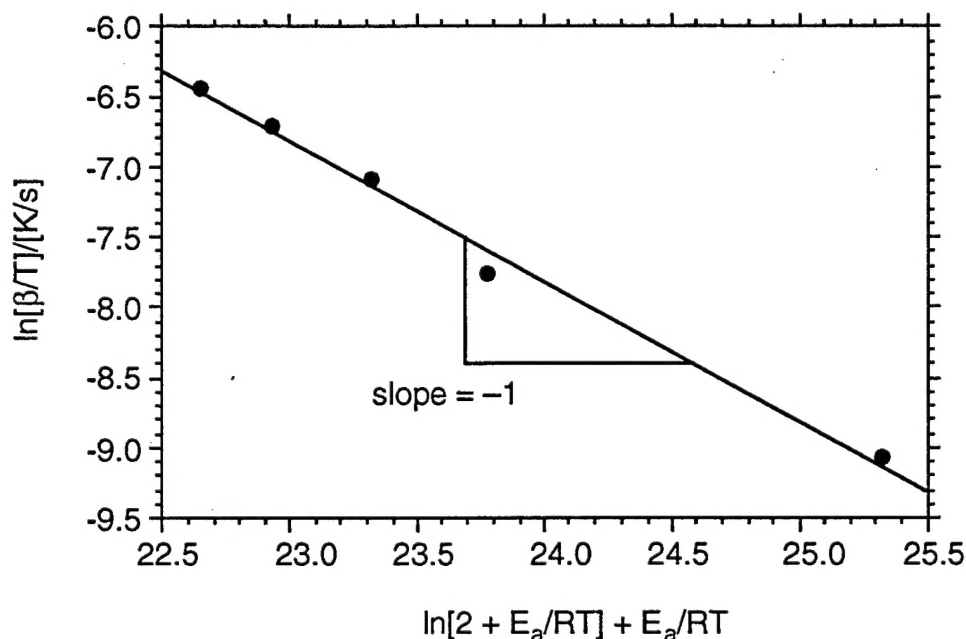


FIGURE 6. PLOT OF $\ln[\beta/T]$ VERSUS $\{\ln[2 + E_a/RT] + E_a/RT\}$ FOR CURE OF PHENYLETHYNYL-TERMINATED IMIDE OLIGOMER AT COMPLETE CONVERSION ACCORDING TO EQUATION 20 WITH $E_a = 133 \text{ kJ/mol}$

CONCLUSIONS

A semianalytic solution of the constant heating rate Arrhenius integral is the basis of a new isoconversion method for determining the activation energy and frequency factor of an arbitrary, single-step reaction from a series of temperature scanning experiments. No assumptions about the form of the rate law are necessary to apply the present integral method to the analysis of non-isothermal reaction data. Thermogravimetry data for a low-density polyethylene at various constant heating rates were analyzed using the new method and the activation energy $E_a = 200$ kJ/mol and the frequency factor $A = 2 \times 10^{11} \text{ s}^{-1}$ determined from the data for anaerobic pyrolysis were in the range of published values for this polymer under these conditions. The new isoconversion method was also used to analyze differential scanning calorimetry data for the curing reaction of phenylethynyl-terminated imide oligomers and provided an activation energy $E_a = 133$ kJ/mol in quantitative agreement with published work. A single value for the frequency factor was obtained for the phenylethynyl curing reaction using the present method $A = 1 \times 10^7 \text{ s}^{-1}$, which is well within the range $A = 10^4\text{--}10^9 \text{ s}^{-1}$ estimated from the original work.

The agreement of the Arrhenius activation energy and frequency factor for polyethylene pyrolysis and the phenylethynyl curing reaction determined by the present method with literature values for these quantities suggests the general utility of the simple new isoconversion integral method for determining kinetic parameters of single-step reactions from constant heating rate experiments. Determination of a physically meaningful reaction rate law from isothermal experiments is now possible since the Arrhenius rate constant can be obtained independent of any assumptions about reaction order or the form of the conversion function $f(\alpha)$.

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